The Nanopore Inner-Sphere Enhancement (NISE) Effect and its Role in Sodium Retention

Dr. Daniel R. Ferreira
Meiji University, Tokyo, Japan
May 12, 2016
Presentation Outline

I. The Nanopore Inner-Sphere Enhancement (NISE) Effect

II. Investigation of the NISE Effect for cation adsorption on zeolites

III. Confirmation of the NISE Effect using NMR / EPR Spectroscopy and Calorimetry

IV. Application of the NISE Effect in a Column Study
Presentation Outline

I. The Nanopore Inner-Sphere Enhancement (NISE) Effect

II. Investigation of the NISE Effect for cation adsorption on zeolites

III. Confirmation of the NISE Effect using NMR / EPR Spectroscopy and Calorimetry

IV. Application of the NISE Effect in a Column Study
Ion Adsorption

Isomorphous substitution creates mineral charge imbalance

Negative charge imbalances balanced by adsorbing cations
Ion Adsorption

Groundwater

Negatively charged mineral surface
Ion Adsorption

Groundwater

Negatively charged mineral surface
Ion Adsorption
Ion Adsorption

The Na and Ca both want to adsorb, but they use different mechanisms.

Outer-Sphere Adsorption  Inner-Sphere Adsorption
Ion Exchange

Stronger ions replace weaker ions.
Weaker ions move from surface to solution.
Nanopores

- Nanopores change the rules of ion adsorption / ion exchange
  - Ionic radius and hydration strength become very important
The Nanopore Effect

- Nanopores change the rules of ion adsorption / ion exchange
- Ionic radius and hydration strength become very important
Presentation Outline

I. The Nanopore Inner-Sphere Enhancement (NISE) Effect

II. Investigation of the NISE Effect for cation adsorption on zeolites

III. Confirmation of the NISE Effect using NMR / EPR Spectroscopy and Calorimetry

IV. Application of the NISE Effect in a Column Study
Zeolites are nanoporous aluminosilicate minerals. The dimensions of the pores are predictable and fixed. This makes zeolites ideal for studying pore size effects.

- **Zeolite Y**: Large pores
  - 0.74x0.74 nm

- **ZSM-5**: Medium pores
  - 0.51x0.55 nm
  - 0.53x0.56 nm

- **Mordenite**: Large & Small pores
  - 0.70x0.65 nm
  - 0.26x0.57 nm

- The dimensions of the pores are predictable and fixed. This makes zeolites ideal for studying pore size effects.
Cation Adsorption on Zeolites

- Adsorption studies were conducted on three zeolites to confirm the NISE model predictions
  - Zeolites mixed in aqueous solution with H₂O, NaOH, and HCl. CaCl₂ and KCl added to some mixtures as competitors.
  - Mixtures were agitated 18-20 hours, then centrifuged.
  - Liquid separated, analyzed for pH and [Na], [Ca], and [K]

<table>
<thead>
<tr>
<th>Charge</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic D (nm)</td>
<td>0.248</td>
<td>0.318</td>
<td>0.240</td>
</tr>
<tr>
<td>ΔG* (kJ mol⁻¹)</td>
<td>-368</td>
<td>-296.5</td>
<td>-1529</td>
</tr>
</tbody>
</table>

Hydration energy values from Hummer et al., 1996. Ionic diameter values from Schulthess, 2005.
Zeolite Y (large pores)

Pore sizes:
Pore 1 – 0.74x0.74 nm

Surface area:
700 m² / g

CEC:
0.09 umol_c / m²

Affinity Sequence: Na ~ Ca ~ K
ZSM-5 (Medium pores)

Pore sizes:
Pore 1 – 0.51x0.55 nm
Pore 2 – 0.53x0.56 nm

Surface area:
425 m² / g

CEC:
0.589 umol_c / m²

Affinity Sequence: K > Na >> Ca
Mordenite (large & small pores)

- **Affinity Sequence:** Ca ~ K > Na

- **Pore sizes:**
  - Pore 1 – 0.70x0.65 nm
  - Pore 2 – 0.26x0.57 nm

- **Surface area:**
  - 500 m² / g

- **CEC:**
  - 0.491 umol_c / m²

- **Surface area:**

**Diagram:**
- Mordenite
- Na⁺
- Na⁺ with Ca²⁺
- Na⁺ with K⁺
- Ca²⁺ with Na⁺
- Ca²⁺
- K⁺ with Na⁺

**Adsorption, µmol m⁻²:**
- pH 0 2 4 6 8 10
- Adsorption, µmol m⁻²:
  - 0.0
  - 0.2
  - 0.4
  - 0.6
  - 0.8
  - 1.0
  - 1.2
  - 1.4
Adsorption studies of Na\(^+\), K\(^+\), and Ca\(^{2+}\) showed:

- **Large pores** – All 3 cations weak
- **Medium pores** – Monovalent cations strong, divalent cation weak
- **Small pores** – All 3 cations strong
Presentation Outline

I. The Nanopore Inner-Sphere Enhancement (NISE) Effect

II. Investigation of the NISE Effect for cation adsorption on zeolites

III. Confirmation of the NISE Effect using NMR / EPR Spectroscopy and Calorimetry

IV. Application of the NISE Effect in a Column Study
Sodium under NMR
Sodium under NMR

Applied Magnetic Field
Sodium under NMR

A transverse magnetic field is applied at a frequency in resonance with precession, creating a torque. They align with the field...
Transverse Magnetic Field is applied at a frequency in resonance with precession, creating a torque.

When the Transverse Magnetic Field is released...
Sodium under NMR

Applied Magnetic Field
The atoms return to their equilibrium states.
NMR Spectra

A - ZSM-5

B - Mordenite

C - Zeolite Y
NMR and Divalent Ions

- NMR can’t analyze metallic elements
- NMR works based on an element’s precession frequency.
  - Difficult to analyze for any of the Group 2 elements due to low precession frequencies
- Need to address adsorption mechanisms of divalent ions on zeolites to completely prove the NISE theory
EPR Spectroscopy

- EPR spectroscopy works like NMR, but on the electrons instead of the nucleus
- The study used a Bruker 380E 9.5 GHz X-band spectrometer with a WD14838 probe on Mn$^{2+}$
EPR Spectroscopy

Mn Adsorption:
Weak on zeolite Y
Weak on ZSM-5
Strong on mordenite
Summary of NMR/EPR

- NMR showed outer-sphere Na adsorption on zeolite Y & inner-sphere Na adsorption on ZSM-5 and mordenite.

- EPR showed outer-sphere Mn adsorption on zeolite Y and ZSM-5 & inner-sphere Mn adsorption on mordenite.

- These data match the predictions of the NISE model.
Calorimetry

- Calorimetry measures the heat of reactions
- Flow calorimetry can compare the heat of exchange between Na and Ca on the zeolite minerals
Calorimetry

Zeolite Y: 0.74 x 0.74 nm

Zeolite Y

Calorimetric Signal, mV

Time, min

- Ca exchanging Na
- Na exchanging Ca
Calorimetry

ZSM-5: 0.51 x 0.55 nm
0.53 x 0.56 nm

Ca$^{2+}$

Na$^+$

![Graph showing calorimetric signal over time for ZSM-5 with two lines: one for Ca exchanging Na and the other for Na exchanging Ca.](image-url)
Presentation Outline

I. The Nanopore Inner-Sphere Enhancement (NISE) Effect

II. Investigation of the NISE Effect for cation adsorption on zeolites

III. Confirmation of the NISE Effect using NMR / EPR Spectroscopy and Calorimetry

IV. Application of the NISE Effect in a Column Study
Sodic Soils

- Sodic soils affect a significant area of the US. Each dot below represents 10,000 acres of sodic soil.
  - ND estimates losses due to sodic soils of $50-$90 million per year
- Sodic soils strongly retain Na to the exclusion of many other ions
- Sodic soils are clay-rich & 2:1 interlayers can reach NISE sizes

From NRCS, c/o Brady & Weil, 2008

Map produced by NRCS based on STRATSGO database
Sodic Soils

- How strongly is Na retained in sodic soils?
Sodic Soils

- Initial desorption experiments on sodic soils showed a Na desorption edge at pH 7 (very weakly held)
- This was likely due to high liquid to solid ratio in batch
Sodic Soils

- As water fills clay interlayers, they expand
- Batch experiments have a high water to solids ratio
- If clays expand, any NISE effect will cease
- Sodic soils tend to be dense and tightly packed
- This would tend to prevent clay interlayer expansion
- A column study can attempt to recreate these conditions
Column Study

- Stainless steel column filled with sand mixed with a Na-montmorillonite. Column is pressurized so clay cannot expand as easily.
- Na retention measured at various clay contents
- [Na] desorbed remained mostly flat with ↑ [clay]
- [Ca] desorbed dropped sharply between 25% and 30% clay
- Pump failed above 30% clay, likely due to low hydraulic cond.
Conclusions

- The NISE effect offers a new model for explaining counterintuitive ion exchange reactions inside small confining environments such as zeolite nanopores
- The predictions of the NISE model have been directly verified through NMR, EPR, and calorimetry
- Attempts to replicate the NISE effect with 2:1 clay interlayers in a column study showed interesting preliminary results. More work is required in this area
References


